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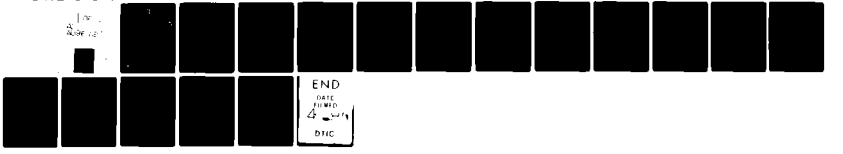

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THE TIME-TEMPERATURE-TRANSFORMATION (TTT) STATE DIAGRAM AND ITS ROLE IN DETERMINING STRUCTURE/PROPERTY RELATIONSHIPS IN THERMOSETTING SYSTEMS

by

J. K. Gillham

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February 1981

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A generalized time-temperature-transformation (TTT) state diagram for the thermosetting process is presented in which the four physical states encountered (i.e., liquid, rubber, ungelled glass and gelled glass) are related to the time and temperature of cure. Gelation and vitrification, as a consequence of quenching morphological development and chemical conversion respectively, are discussed with respect to control of material properties.

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ABSTRACT

A generalized time-temperature-transformation (TTT) state diagram for the thermosetting process is presented in which the four physical states encountered (i.e., liquid, rubber, ungelled glass and gelled glass) are related to the time and temperature of cure. Gelation and vitrification, as a consequence of quenching morphological development and chemical conversion respectively, are discussed with respect to control of material properties.

TIME-TEMPERATURE-TRANSFORMATION (TTT) STATE DIAGRAMS

Recent research (1-5) has indicated that a Time-Temperature-Transformation diagram (analogous to the TTT diagrams that have been employed for many years in metallurgical processing) may be used to provide an intellectual framework within which an understanding of the physical properties of thermosetting matrices may be achieved.

Figure 1a (3) shows a generalized TTT diagram obtained from isothermal experiments for a typical thermosetting process that does not involve phase separation. It displays the four distinct material states (liquid, elastomer, ungelled glass and gelled glass) that are encountered during cure. Three critical temperatures are also displayed on the diagram. These are $T_{g\infty}$, the

maximum glass transition temperature of the fully cured system, ${}_{gel}T_g$, the isothermal temperature at which gelation and vitrification occur simultaneously, and ${}_{resin}T_g$, the glass transition temperature of the reactants.

When a thermosetting material is cured isothermally above $T_{g\infty}$, the liquid gels to form an elastomer but it will not vitrify in the absence of degradation. (Vitrification due to degradation is shown in Fig. 1). An isothermal cure at an intermediate temperature between ${}_{gel}T_g$ and $T_{g\infty}$ will cause the material first to gel and then to vitrify. If chemical reactions are quenched by vitrification it follows that the glass transition temperature will then equal the temperature of cure and that such a material will not be fully cured. At temperatures below ${}_{gel}T_g$ but above ${}_{resin}T_g$ the viscous curing liquid can vitrify simply by an increase of molecular weight and, if chemical reactions are quenched by vitrification, the material need not gel.

It is immediately apparent that structure-property relationships will only be meaningful if the material is fully reacted. This is generally only possible by curing above $T_{g\infty}$.

As indicated in Fig. 1 the time to vitrify passes through a minimum between ${}_{gel}T_g$ and $T_{g\infty}$. This behavior reflects the competition between the increased rate constant for reaction and the increasing chemical conversion required to achieve vitrification as the temperature is increased. Also, as indicated in Fig. 1, the time to vitrify passes through a maximum between ${}_{resin}T_g$ and ${}_{gel}T_g$. This behavior reflects the competition between the temperature and time dependence of viscosity of the reacting system.

The cure TTT diagram of Fig. 1a can be extended (see Fig. 1b) to include two phase systems such as the rubber-modified thermosets used to

improve the toughness of glassy state thermosets. The curing of such rubber-modified systems may involve a change from an initially homogeneous solution to a heterogeneous morphology with dispersed rubber. Figure 1b includes the locus of the visual onset of phase separation. Gelation may arrest the development of the rubber second phase and therefore procedures which alter the time and temperature to gelation can be used to control the material properties. Control of the time-temperature history of the material during cure is a method of achieving the desired degree of phase separation, but a knowledge of the TTT diagram is prerequisite for such a procedure. Since the nucleation and growth of the rubber phase involves a balance between nucleus formation and matter transport, the degree of phase separation achieved in an isothermal process would be expected to show a maximum at a temperature between that for which thermodynamics favors the solubility of the rubber in the matrix and the $_{resin}T_g$ of the matrix (6). Careful control of the cure temperature will also permit the size and number of particles per unit volume of the dispersed rubber phase to be modified and hence have a strong effect on the mechanical properties. Evidence has been presented (6,7) to show that improved material toughness arises in rubber-modified systems in which part of the rubber is phase-separated and part is trapped "in solution" in the matrix. The path taken on the TTT diagram must therefore be chosen so as to balance the distribution of the rubber between the two phases.

A continuous Heating Transformation (CHT) State Diagram (not shown) which is analogous to the isothermally obtained TTT state diagram can be obtained experimentally from a series of temperature scans at different rates from below the glass transition temperature of the reactants ($_{resin}T_g$) to above $T_{g\infty}$. A typical scan for a homogeneous reactive system will reveal in

sequence: relaxations in the glassy state, $_{resin}T_g$, gelation, vitrification, revitrification
^and (in the presence of some types of degradation) revitrification. After vitrification on cure, in these scans, the glass transition temperature will in principle equal the instantaneous scanning temperature until the rate of chemical reaction is not sufficient to overcome the increased segmental mobility of the developing network, at which temperature the material will devitrify.

TORSIONAL BRAID ANALYSIS (TBA) - A METHOD FOR CONSTRUCTING TTT & CHT STATE DIAGRAMS

An automated, free-hanging, freely decaying torsion pendulum has been developed (1,8) which permits monitoring of the changes which occur throughout cure by using a support (e.g. braid) impregnated with the reactive system (TBA).

The TTT diagram (Fig. 1a) can be generated by measuring times to gel and to vitrify at a series of isothermal temperatures. These transformation times have been obtained using TBA from measurements of peaks in the mechanical damping as a function of time which correspond to points of inflection in the rigidity curves. Complementary CHT diagrams have been generated by scanning the temperature range from below the glass transition temperature of the reactant mixture, $_{resin}T_g$, to above $T_{g\infty}$ at a series of constant heating rates.

Details of procedures and results on structure-property relationships of thermosetting systems are provided in recent publications (1-12).

An advantage of a freely suspended torsion pendulum specimen over forced systems is its sensitivity which is the consequence of the free end.

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This has led to the revelation of fine details in the dynamic mechanical spectra which suggest, for example, that gelation is a multistep process (4,10,11).

EFFECT OF EXTENT OF CURE ON MATERIAL BEHAVIOR

In principle, cure at a temperature T_{cure} which is below $T_{g\infty}$ will lead to the glass transition temperature $T_g = T_{cure}$. Post-cure above $T_{g\infty}$ will lead to $T_g = T_{g\infty}$. An epoxy was cured according to the manufacturer's specifications and yielded the thermomechanical TBA behavior "before post-cure" shown in Fig. 2 (which lists experimental details and a summary of transitions). It is apparent that the cure cycle was not sufficient to have $T_g = T_{cure}$. Post-cure resulted in significant increase in T_g as well as change in the viscoelastic behavior (e.g., the damping behavior) below the glass transition. In particular, a small but significant decrease in the rigidity (i.e. modulus if no dimensional changes occur on post-cure) occurred in the glassy state at, for example 0°C (0mV, Fig. 2) in consequence of the post-cure. This is a result of the non-equilibrium nature of the glassy state. Cooling at the same rate through a glass transition leads to a supercooled liquid which is further from equilibrium at, e.g. 0°C, the higher the T_g.

Consider (Fig. 3) two specimens (1 and 2), one cured above $T_{g\infty}$ at temperature ${}_2T_{cure}$, the other cured below $T_{g\infty}$ at temperature ${}_1T_{cure}$. Specimen 1 vitrified on cure to give a glass transition equal to the temperature of cure. Specimen 2 reacted completely to give the maximum glass transition temperature ($T_{g\infty}$). In the hypothetical absence of further reaction above temperature ${}_1T_{cure}$ the specific volume of the specimen cured at the lower temperature will be higher at ${}_2T_{cure}$ than that cured at ${}_2T_{cure}$ (due to lower crosslink density and more unreacted ends). The

diagram, Fig. 3 (13), shows that cooling of the more completely reacted material (at equal rates) results in a higher T_g and indicates how a higher specific volume may result in the glassy state. The fundamental reason is that the material with the higher T_g is further from equilibrium at e.g. room temperature (RT).

The higher free volume at RT of the more highly crosslinked material is held responsible for its lower density and lower modulus at RT and greater water absorption on immersion at RT (5,13).

EFFECT OF GELATION ON MATERIAL PROPERTIES IN TWO-PHASE SYSTEMS

The influence of gelation time on morphology is made evident by comparison of the thermomechanical TBA behavior of a rubber-modified epoxy cured without (Fig. 4a) and with (Fig. 4b) catalyst (12). The glass transition temperature of the rubber is much more dominant in the sample cured without catalyst. This suggests that the extent of phase separation depends on the time available for phase separation which is limited by the process of gelation. The higher glass transition temperature of the epoxy for the sample cured with the longer gelation time also suggests more complete separation of the two phases.

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FIGURE CAPTIONS

Fig. 1. Schematic Time-Temperature-Transformation (TTT) diagrams obtained isothermally for the curing process. a) A thermosetting system not involving phase separation. b) A thermosetting system in which a rubber phase may separate during cure. The visual onset of phase separation (the "cloud point") is indicated. (T_s is the maximum temperature for phase separation to occur prior to gelation.)

Fig. 2. Thermomechanical behavior (TBA) of an epoxy after recommended cure and after post-cure. Note the decreased rigidity at 0°C (0mV) after post-cure.

Fig. 3. Schematic: Specific volume versus temperature in the absence of chemical reaction. Cured at temperature $_1T_{cure}$: dashed line. Cured at temperature $_2T_{cure}$: solid line. Note the higher specific volume at room temperature (RT) of the more highly reacted system.

Fig. 4. Thermomechanical behavior (TBA) of an epoxy-rubber system following identical time-temperature cure paths. a) Zero parts per hundred of catalyst. b) 0.5 parts per hundred of catalyst.

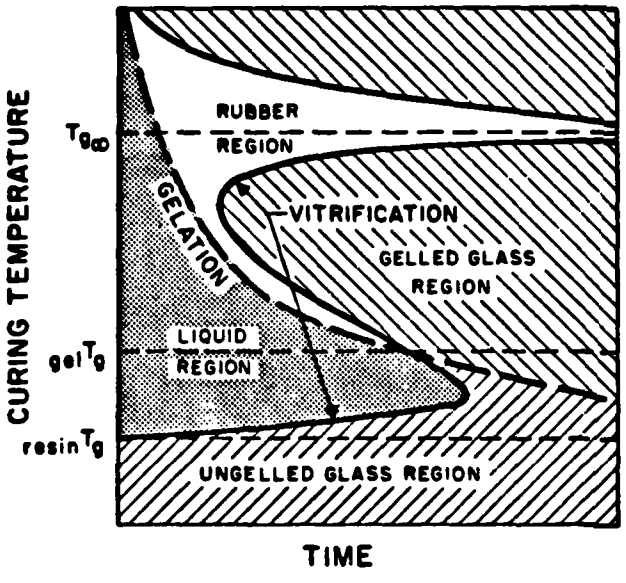
CURING TEMPERATURE
$T_{g\infty}$
RUBBER
REGION
GELATION
VITRIFICATION
GELLED GLASS
REGION
LIQUID
REGION
$gel\,T_g$
$resin\,T_g$
UNGELLED GLASS REGION
TIME

Fig. 1a

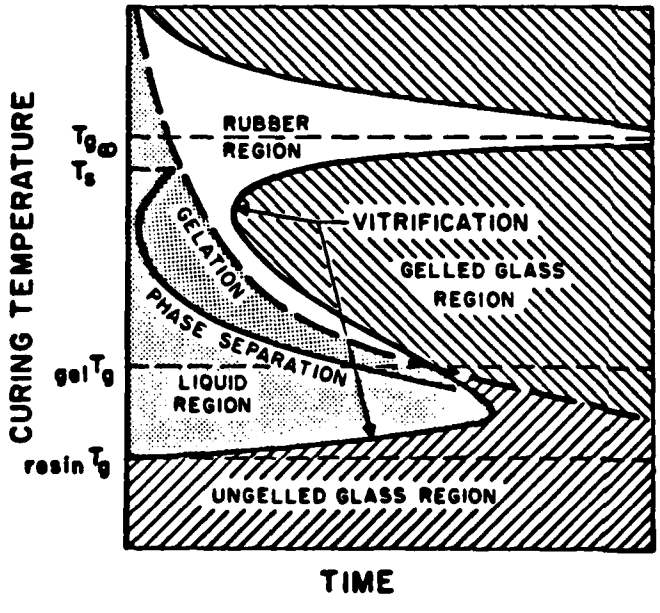
CURING TEMPERATURE
$T_{g\infty}$
T_s
RUBBER
REGION
GELATION
VITRIFICATION
GELLED GLASS
REGION
PHASE SEPARATION
LIQUID
REGION
$gel\,T_g$
$resin\,T_g$
UNGELLED GLASS REGION
TIME

Fig. 1b

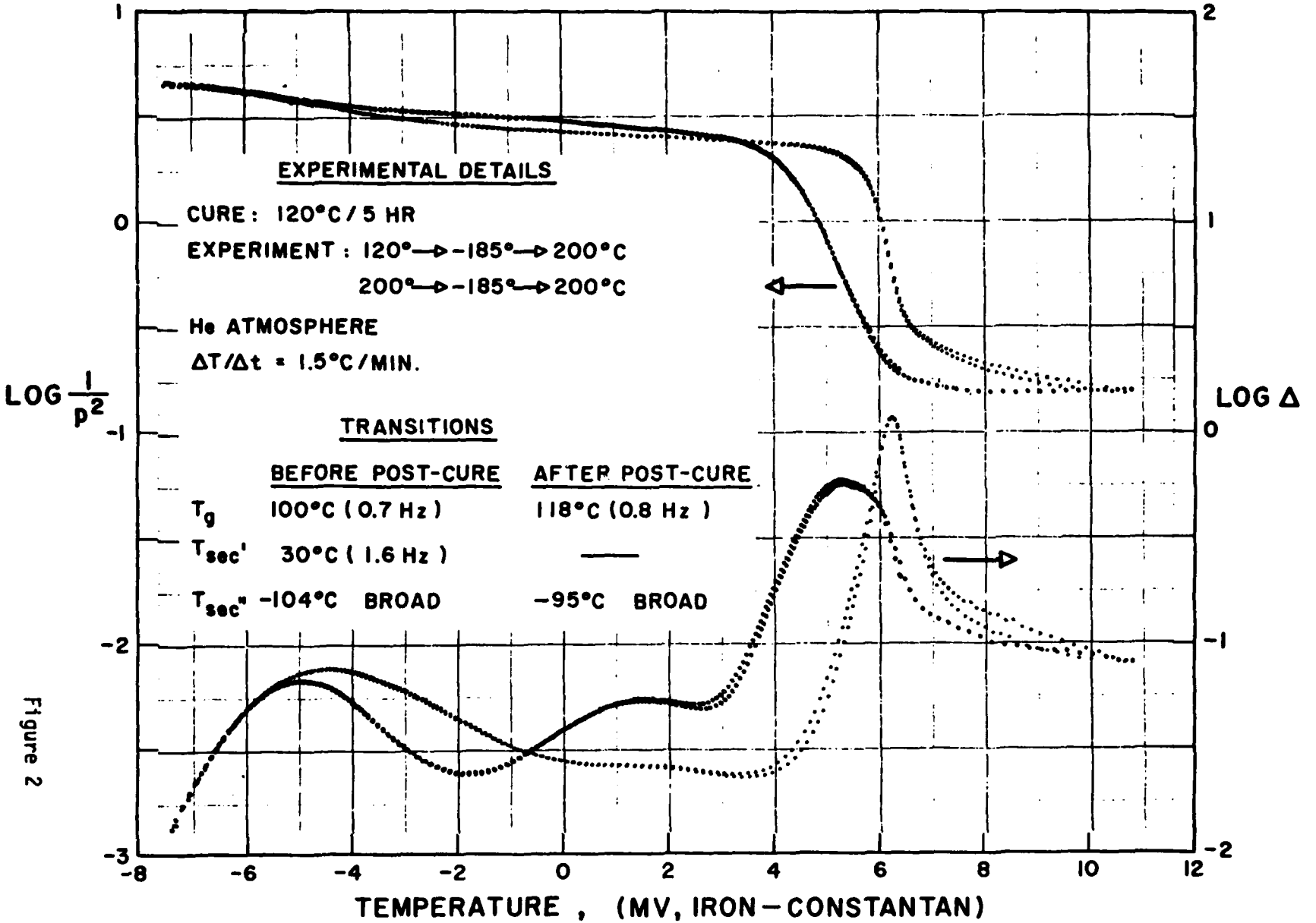
EXPERIMENTAL DETAILS
CURE : 120°C / 5 HR
EXPERIMENT : 120° → -185° → 200°C
200° → -185° → 200°C
He ATMOSPHERE
ΔT/Δt = 1.5°C/MIN.
TRANSITIONS
BEFORE POST-CURE
AFTER POST-CURE
Tg 100°C (0.7 Hz) 118°C (0.8 Hz)
Tsec' 30°C (1.6 Hz) ——
Tsec" -104°C BROAD -95°C BROAD
LOG 1/p²
LOG Δ
TEMPERATURE , (MV, IRON-CONSTANTAN)
1
0
-1
-2
-3
2
1
0
-1
-2
-8
-6
-4
-2
0
2
4
6
8
10
12

Figure 2

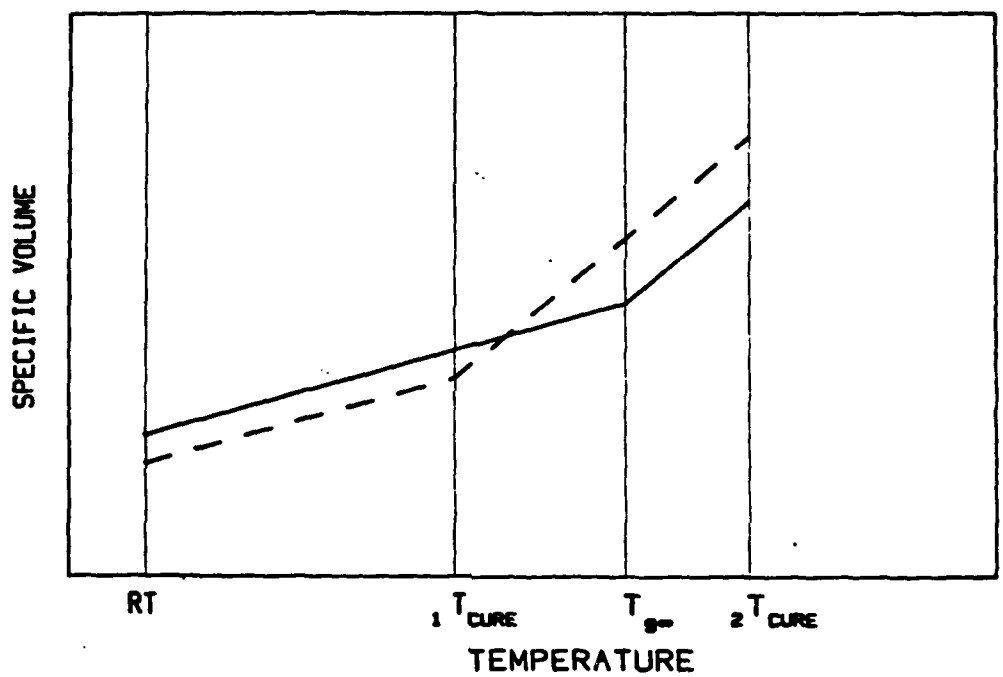

Fig. 3

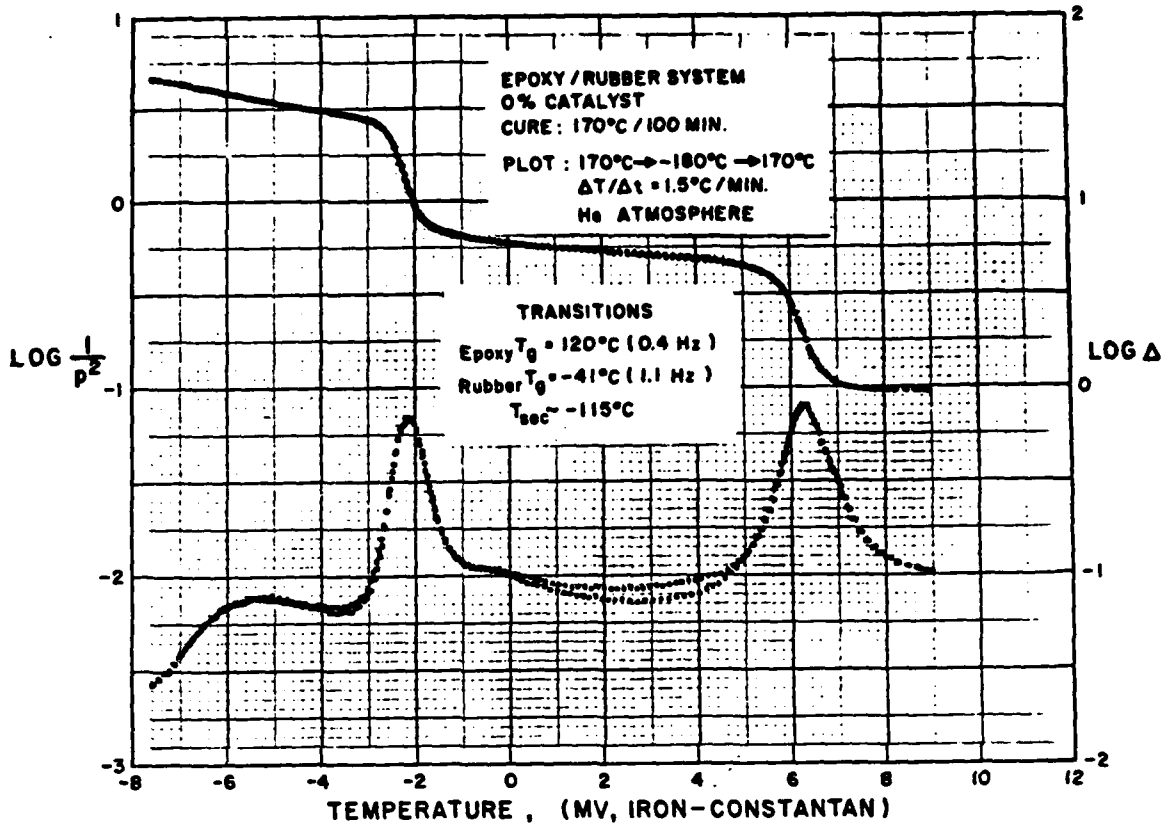
EPOXY / RUBBER SYSTEM
0% CATALYST
CURE : 170°C / 100 MIN.
PLOT : 170°C → -180°C → 170°C
ΔT/Δt = 1.5°C / MIN.
He ATMOSPHERE
TRANSITIONS
Epoxy Tg = 120°C (0.4 Hz)
Rubber Tg = -41°C (1.1 Hz)
Tsec ~ -115°C
LOG 1/p²
LOG Δ
TEMPERATURE , (MV, IRON-CONSTANTAN)

Fig. 4a

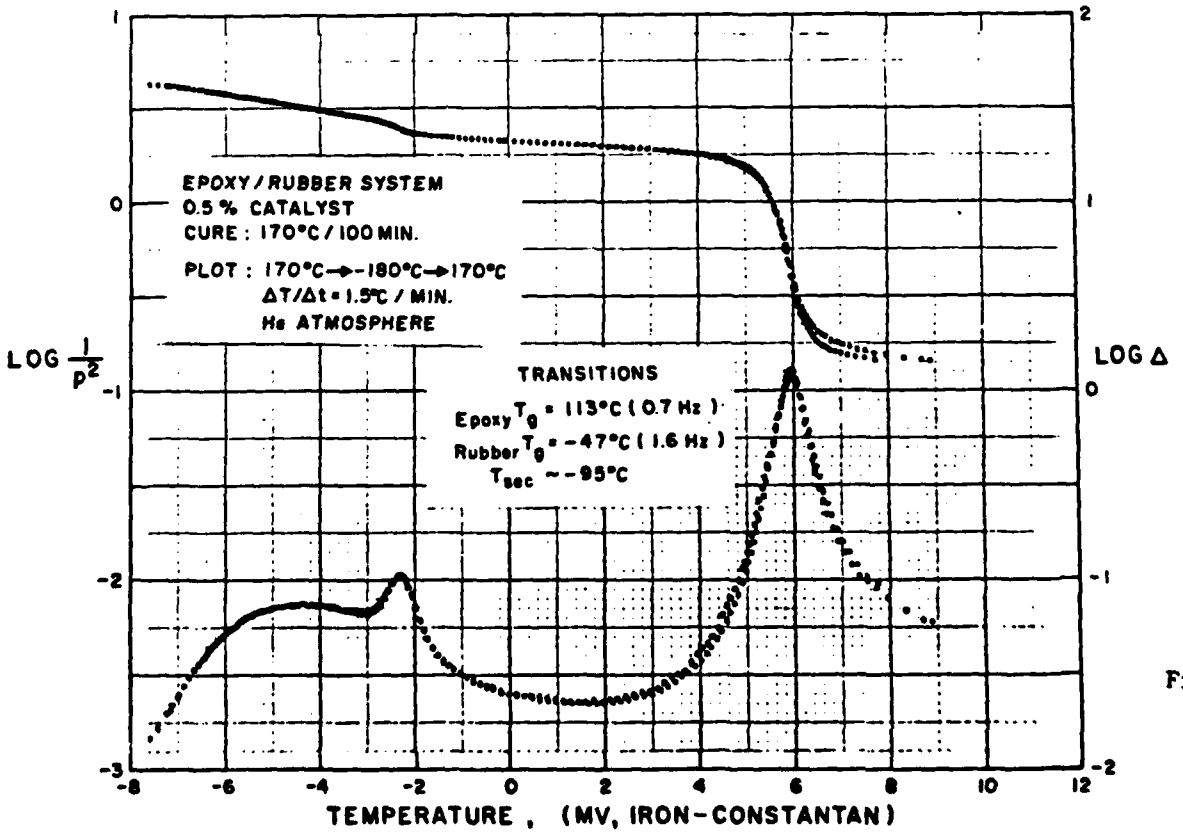
EPOXY / RUBBER SYSTEM
0.5 % CATALYST
CURE : 170°C / 100 MIN.
PLOT : 170°C → -180°C → 170°C
ΔT/Δt = 1.5°C / MIN.
He ATMOSPHERE
TRANSITIONS
Epoxy Tg = 113°C (0.7 Hz)
Rubber Tg = -47°C (1.6 Hz)
Tsec ~ -95°C
LOG 1/p²
LOG Δ
TEMPERATURE , (MV, IRON-CONSTANTAN)

Fig. 4b

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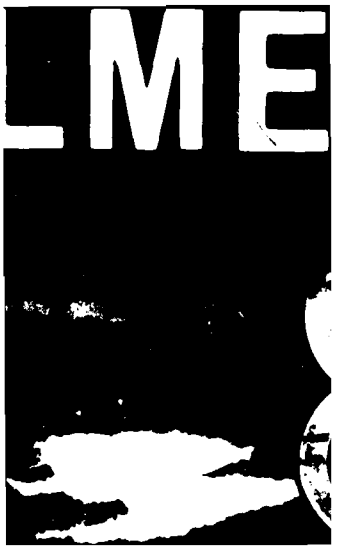
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